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U. S. GEOLOGICAL SURVEY
George Otis Smith, Director

BULLETIN 778

CHEMISTRY OF DEPOSITION OF NATIVE COPPER FROM ASCENDING SOLUTIONS

BY

ROGER C. WELLS

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Experiment 44.—Ferric oxide and cuprous sulphide at 300° C. Initial weights: Fe_2O_3 0.24 gram, Cu_2S (prepared by heating copper sulphide in hydrogen at 600° for an hour and found by analysis to be Cu_2S) 0.0796 gram, H_2O 5 grams, and CO_2 to displace air. The experiment was first tried in glass tubes, which were heated in an iron bomb containing water to equalize the pressure within the tubes, but the glass tubes were so badly attacked and decomposed that the results were useless. Silica tubes were then substituted for the glass. At first these were placed in larger glass tubes containing water, as the first tubes available were rather thin. However, the alkaline solution formed from the glass also attacked the silica. Later strong silica tubes were obtained and heated directly in the steel bomb with water to equalize the pressure. Heated in silica tubes at 300° for 2 hours; no visible change. Heated at 300° for 3 days; no visible change, except that some of the silica formed a colloidal solution and some was deposited at the bottom of the solution. Cu_2S remained unchanged. No sulphate was formed.

Experiment 45.—Initial weights: Fe_2O_3 0.080 gram, Cu_2S 0.1592 gram, H_2O and CO_2 as in experiment 44. Results same as those in experiment 44.

Experiment 46.—Action of sulphur dioxide on cupric sulphate solutions at 160° C. Initial weights: $CuSO_4.5H_2O$ 0.79 gram=0.2 gram Cu, SO_2.aq. 2.9 cubic centimeters=0.19 gram SO_2, H_2O 1.0, air about 5 cubic centimeters. Warmed to 100°; spangles of copper became visible. Heated to 160° for 1 hour; SO_2 used up 0.14 gram, Cu precipitated 0.125 gram.

Experiment 47.—Similar to experiment 46. Initial weights: $CuSO_4.5H_2O$ 0.79 gram, SO_2 0.30 gram in 4.75 cubic centimeters. Heated for 1 hour at 160°. Copper estimated still in solution from color, 0.04 gram. Heated at 200° a moment, then 19 hours at 160°. Solution still blue, but the copper had a black film on it.

Experiment 48.—Action of sulphur dioxide on copper. Weights: Copper 2.9530 grams, SO_2 5 cubic centimeters=0.305 gram. Heated at 145° for 21 hours; a few brownish flocs suggesting a sulphide. Heated for 21 hours more; same result. Heated at 217° for 42 hours; a lot of black sediment. SO_2 remaining, 0.020 gram; used, 0.285 gram; SO_4 formed=0.125 gram H_2SO_4. Copper remaining, 2.8434 grams; changed to Cu_2S, 0.1096 gram.

Experiment 49.—Action of dilute sulphuric acid on copper. A little copper was heated with 10 cubic centimeters 0.5 normal sulphuric acid in a sealed tube free from air to 200° for 42 hours. No color could be detected in the solution, and the copper remained bright. Analysis gave 0.08 milligram in the solution, equivalent to 8 milligrams per liter. See experiment 138 for results at 300°.

Experiment 50.—Resembled 38*b*. Initial weights: Fe_2O_3 about 0.15 gram in the form of a suspension, $CaCO_3$ 0.05 gram, H_2O 25 cubic centimeters. Air boiled out. Cu_2S added, 0.15 gram. CO_2 was passed for 1 hour, and tube was sealed without interrupting stream of CO_2. Heated at 92° for 23 days. Practically no sulphate formed. Residue warmed with dilute HCl, filtered off; the solution showed ferrous iron and cupric salt but no sulphate.

Experiment 51.—Experiment 51 was similar to the preceding experiment. Initial weights: Fe_2O_3 0.08 gram, Cu_2S 0.1592 gram, $CaCO_3$ 1.27 grams, HCl (in inner tube) 0.92 gram. Volume of tube 26.5 cubic centimeters. Heated at about 150° for 17 days; considerable black and some purple precipitate formed. No further significant changes were noted during the course of 27 days further heating. No metallic copper was observed.

Experiment 52.—Action of copper on hydrochloric acid. Taken: 10 cubic centimeters 0.5 normal acid, 3.0 grams copper wire, in tube with atmosphere of CO_2. Heated 2 days at 150°, then 17 hours at 165°. Some of the copper was dissolved and reprecipitated on one end of the wires. The solution, after cooling, gave the equivalent of 0.70 gram copper per liter.

Experiment 52a.—An apparatus, shown in Figure 1, was arranged by which a concentrated solution of cuprous chloride, dissolved in strong calcium chloride, could be diluted with pure water, all in an atmosphere of CO_2. Only a few drops were mixed every few days by allowing some of the mixture to escape while first water and then cuprous chloride entered the long tube in which mixing occurred. During the course of six months a noteworthy deposit of crystals of copper formed where the first dilution occurred. Cuprous chloride was also deposited. At the second point of dilution these phenomena were less conspicuous. A long copper wire had been placed in the tube to see if any electrolytic transfer would occur, but the results appeared to be due entirely to the dilution of the concentrated solution.

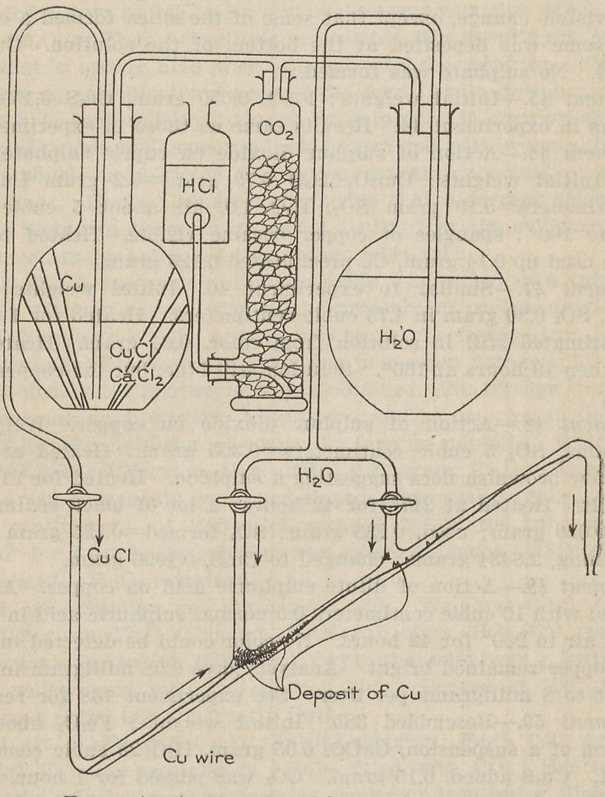

FIGURE 1.—Apparatus used in experiment 52*a*

Experiment 53.—Copper and mine water from 81st level, Red Jacket shaft, Calumet & Hecla mine, depth 4,900 feet, collected August, 1921. Some metallic copper was heated with 20 cubic centimeters of this water at 92° in a glass tube for 3 months. Copper found in solution 0.2 milligram, equivalent to 0.01 gram per liter.

Experiment 54.—Experiment 54 was similar to the preceding one, with an atmosphere of CO_2. Heated at 150° for 40 days; 15 cubic centimeters of the solution gave 1.8 milligrams of copper equivalent to 0.12 gram per liter.

Experiment 55.—Solubility of copper in calcium chloride brine (equal parts $CaCl_2$ and H_2O). Heated at 175° for 20 hours and filtered hot; the solution gave the equivalent of 0.07 gram of copper per liter.

Experiment 56.—Similar to preceding. Initial weights: $CaCl_2.H_2O$ 15.0 grams, H_2O 12.0 grams, Cu 3.0 grams, Fe_2O_3 0.2 gram, SiO_2 0.2 gram. Heated at 200° about 2 days; the solution gave the equivalent of 0.19 gram of copper per liter.

Experiment 57.—Solubility of copper in the presence of acid and Fe_2O_3. Initial weights: Fe_2O_3 0.2 gram, HCl 0.1 gram, H_2O 15.0 cubic centimeters; copper in excess. Heated at 90° for 3 days; the solution gave 0.042 gram of iron in the ferrous state and 0.017 gram copper=1.3 gram per liter.

Experiment 58.—Repetition of experiment 35. Initial weights: Cu_2S 0.250 gram, H_2SO_4 (boiled) 1.50 grams. Heated in an evacuated sealed tube at 200° for 4 days; the Cu_2S disappeared. Volume of tube 9.3 cubic centimeters. Pale-blue crystals, probably a sulphate of copper, perhaps $CuSO_4.3H_2O$, formed. Opened under iodine solution, the SO_2 formed was estimated by titration to be 0.32 gram after allowing for the iodine liberated from the KI by the $CuSO_4$. The following equation is suggested:

$$Cu_2S+6H_2SO_4=5SO_2+2CuSO_4+6H_2O \qquad (35)$$

This demands 0.50 gram SO_2 calculated from the weight of Cu_2S taken, which is somewhat larger than the SO_2 found. A little SO_2 may have escaped when the tube was opened, however, as the pressure was considerable, and some iodine solution had to be added while the SO_2 was being absorbed, whereas the iodine solution should have been in excess.

Experiment 59.—Similar to experiment 48. Initial weights: Cu 1.999 grams, SO_2 2 cubic centimeters=0.1830 gram, H_2O 3.0 cubic centimeters. Heated 4 days at 225°; considerable Cu_2S formed. SO_2 remaining, 0.029 gram; SO_4'' formed, 0.0770 gram. Apparently 0.0009 gram of sulphur was also formed.

Experiment 60.—Similar to preceding, with the addition of 0.46 gram Fe_2O_3. Heated for 4 days at 225°; only a little Cu_2S formed. No SO_2 remained. $FeSO_4$, 0.214 gram. Sulphur, none. Solution neutral.

Experiment 61.—Sulphur dioxide and cupric sulphate. Initial weights: $CuSO_4.5H_2O$ 0.100 gram, SO_2 5 cubic centimeters=0.158 gram, a little CO_2. Volume of tube 9.6 cubic centimeters. Heated at 225° for 4 hours, the copper first deposited became coated with Cu_2S. Heated at 225° for 5 days, much Cu_2S was formed and in one end of the tube droplets of sulphur. Sulphur found, 0.0084 gram. No H_2S or copper. Trace of SO_2. Reaction acid. SO_4 found, 0.2082 gram. Two reactions probably occur:

$$5SO_2+2CuSO_4+6H_2O\rightleftarrows 6H_2SO_4+Cu_2S \qquad (63)$$

and

$$8SO_2+2CuSO_4+8H_2O=8H_2SO_4+Cu_2S+S \qquad (64)$$

Experiment 62.—Action of cupric sulphate on cuprous sulphide. Initial weights: Cu_2S 0.080 gram, $CuSO_4.5H_2O$ 0.500 gram, H_2SO_4 0.200 gram, H_2O 5 cubic centimeters. Heated at 230° for 1 day; showed numerous flakes of copper on cooling. The second day a very small quantity of an insoluble white salt appeared which was observed in several similar experiments and is believed to be formed by attack of the glass.

Third day, no appreciable change. The results of analyses of the solid residue and final solution obtained are given in Tables 8 and 9. These determinations were made by Prof. Glenn V. Brown, of Bucknell University, to

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whom the writer wishes to express his appreciation for the attention given by him to possible sources of error in the analytical work. Professor Brown also analyzed the products obtained in experiments 69, 101, 102, 104, 108, 110, 114, 115, 116, 117, 121, 123, 125, 127, 128, 132*b*.

Experiment 63.—Qualitative experiment. A mixture of CuS with a solution containing $FeSO_4$, $CuCl_2$, and HCl was heated at 130° for 15 hours. Cu_2S and CuCl were formed. No further change was noted after heating at 200° for two days.

Experiment 64.—Experiment 64 resembled experiment 62 except in the use of 0.69 gram of H_2SO_4. Two days' heating at 200° produced no metallic copper. Four days' further heating some months later, at 300°, yielded considerable copper on cooling.

Experiment 65.—Similar to experiment 62, but with $CaCl_2$ present. (See Table 8.) Heated at 200° for 1 day; no copper formed, but the color of the solution disappeared, and CuCl may have been precipitated in the $CaSO_4$ present.

Experiment 66.—Action of cupric sulphate on cuprous sulphide, continuing experiment 62. Initial weights: Cu_2S 0.080 gram, $CuSO_4.5H_2O$ 0.250 gram, H_2O 5.0 cubic centimeters. Heating at 150° two hours caused the precipitation of considerable basic salt. Heated at 200°; no copper was observed the first day, but some appeared the second day, also possibly Cu_2O. The third day there was more Cu_2O, and all the other constituents were still present. The same result the next day, possibly CuO in addition. Some sulphide was still present. The tube was accidentally broken at this stage, and contents lost.

Experiment 67.—Similar to experiment 66, except with 0.500 gram $CuSO_4.5H_2O$, and 0.100 gram H_2SO_4 in a total volume of 5 cubic centimeters. Heated at 200°. A little copper and basic salt appeared the first day on cooling; somewhat more copper the second day. After 9 days there was no further visible change. The crystals of copper were easily observable with a lens.

Experiment 68.—Copper introduced with the other reagents. Initial weights: Cu_2S 0.08 gram, $CuSO_4.5H_2O$ 0.50 gram, H_2SO_4 0.23 gram, Cu 0.066 gram, H_2O about 5.0 centimeters. Heated at 200° for 1 day; considerable copper appeared as beautiful crystals, on cooling, on the surface of the solution. Heated 24 hours more; even more copper was recrystallized and the wire was about half gone.

Experiment 69.—Will cuprous salts oxidize cuprous sulphide? Initial weights: Cu_2S 0.08 gram, CuCl 0.20 gram, Cu 0.10 gram, H_2O 5.0 cubic centimeters. Heated 6 days at 200°; a little Cu_2O was formed and a little copper was apparently dissolved and reprecipitated on the glass and throughout the solution. No SO_4'' was formed. For the results at 250° see experiment 126.

Experiment 70.—Action of H_2SO_4 on Ag_2S. Initial weights: Ag_2S 0.50 gram, H_2SO_4 (concentrated) 2.0 cubic centimeters, H_2SO_4(1–1) 0.4 cubic centimeters. Heated at 92°, some gas was formed. Heated at 200° for 20 hours; some Ag_2S still remained. The tube showed the presence of SO_2 on opening. The solution gave a precipitate of Ag_2SO_4 on dilution. Found in the solution: SO_2 0.11 gram, Ag 0.1772 gram. Possible reaction:

$$Ag_2S+4H_2SO_4=Ag_2SO_4+4SO_2+4H_2O \qquad (65)$$

Experiment 71.—Uncompleted.

Experiment 72.—Will $FeSO_4$ act on Cu_2S to produce copper? Weights: $FeSO_4.7H_2O$ 0.50 gram, Cu_2S 0.02 gram, H_2O 4.78 cubic centimeters. Heated at 200° 6 days; no significant change was noticed. Some months later the tube was heated 3 days more at 250° without any results.

Experiment 73.—Action of dry cupric chloride on cuprous sulphide. Weights taken: $CuCl_2$ 0.270 gram, Cu_2S 0.159 gram. Sealed in a vacuum and heated to 500° C. for 20 minutes. The mixture melted. Some sulphur sublimed into the ends of the tube. The melt was dark in the center and brown around the edges. Heated again 30 minutes. The melt was clear to brownish black in transmitted light. The sulphur found by extraction with CS_2 was 0.0070 gram. According to this result only part of the materials reacted, and on dissolving the residue in ammonia much Cu_2S appeared which had not been attacked. The ratio of copper to chlorine in the soluble part showed that about 36 per cent of the copper was in the form of cuprous chloride. These findings support the view that as far as the materials reacted the reaction was

$$2CuCl_2+Cu_2S=4CuCl+S \qquad (66)$$

Experiment 74.—Action of sulphur dioxide and hydrogen on copper at 900° C. About 10 grams of copper in the form of a bundle of small wires was heated gradually to 900° during the course of 80 minutes in a stream of gas consisting of about 2 volumes hydrogen to 1 volume sulphur dioxide. Water was formed, but no hydrogen sulphide could be detected in the outgoing gas. After cooling and opening the tube the copper was seen to be converted into beautiful crystals of the sulphide for about a seventh of its length. The crystals were black, blue, brass-colored, lavender, and pale green, very well crystallized, and had apparently been very nearly if not wholly melted. A little bunch of crystals terminated the end of each wire.

Experiment 75.—Will SO_2 convert Cu_2S to copper? Weights: Cu_2S 0.02 gram, SO_2 as dry gas 0.10 gram. Volume of tube 9 cubic centimeters. Heated at 92°, 150°, 200° for 1 day each; no copper was formed.

Experiment 76.—Will SO_2 reduce Fe_2O_3? Weights: Fe_2O_3 0.020 gram, SO_2 as dry gas 0.100 gram. Heated a day at 92°; no change was visible. Heated a day at 150°; the color turned to buff. Heated a day at 200°; no further change. On opening several months later SO_2 was still present under pressure, but the Fe_2O_3 was not all reduced. In fact, on washing out the SO_2 with H_2O, dissolving in H_2SO_4, and titrating with $KMnO_4$ only 0.0020 gram FeO was found.

Experiment 77.—SO_2 and Cu_2S with Fe_2O_3. Weights: Cu_2S 0.020 gram, Fe_2O_3 0.04 gram, SO_2 0.024 gram, H_2O 5.0 cubic centimeters. Heated at different temperatures, finally at 250° for 6 days; no copper was observed.

Experiment 78.—Similar to experiment 77. Weights: Cu_2S 0.02 gram, Fe_2O_3 0.13 gram, SO_2 0.04 gram, $FeSO_4.7H_2O$ 0.5 gram, H_2O 5.0 cubic centimeters. Heated at 200° 2 days; no copper was observed. The solid remained red.

Experiment 79.—Action of liquid sulphur dioxide on cuprous sulphide. Half a gram of SO_2 was condensed into a tube, previously evacuated, containing 0.02 gram Cu_2S, and sealed off. No action could be observed on standing or after the tube was heated 24 hours at 65° C.

Experiment 80.—Action of liquid dioxide on ferric oxide. Ferric oxide was also treated as described in experiment 79. The red color turned slightly paler, somewhat buff, but by no means disappeared.

Experiment 81.—Attempt to increase the action of Cu_2S by increasing its solubility. Initial weights: Cu_2S 0.02 gram, KCN 0.05 gram, Fe_2O_3 0.04 gram, H_2O 5.0 cubic centimeters, SiO_2 0.02 gram. No change resulted after heating at

92° for a day. On heating one day at 200° a dirty black precipitate formed, the Fe_2O_3 was no longer visible, and after long standing a few extremely faint indications of metallic copper were observed. On heating to 250° a year later the tube exploded. Old tubes are apparently considerably weaker than new ones.

Experiment 82.—Behavior of colloidal Cu_2S. Some CuCl was precipitated with H_2S. After washing by decantation about 8 times with water containing H_2S a colloidal solution resulted. Fe_2O_3 was precipitated and washed until it was more or less colloidal. (See experiment 6.) Equal volumes of these two colloidal solutions were mixed and sealed in an atmosphere of CO_2, and the mixture was heated at 92° for 15 days. A green sediment formed, and the solution cleared completely. This result can probably be ascribed to the action of the CO_2 and also to the coagulating effect of one colloid on the other.

Experiment 83.—Initial weights: Fe_2O_3 0.0028 grams, colloidal Cu_2S 15 cubic centimeters. Heated in CO_2 at 200° for 1 day; the red oxide disappeared and a few black flocs were formed. On further heating the tube broke.

Experiment 84.—Action of colloidal Cu_2S on Fe_2O_3. A long tube in the form of a siphon 6 millimeters in diameter was filled with hematite and Fe_2O_3, and through it was caused to pass very slowly a colloidal solution of Cu_2S, which was protected by an atmosphere of CO_2. In the course of some months certain stains that suggested chalcopyrite, bornite, covellite, and, it is barely possible, copper resulted, but the amounts were extremely small and could not be readily observed. The most noticeable effect was that the colloidal Cu_2S was precipitated and retained by the hematite, so that the outflowing solution was clear.

Experiment 85.—Action of cuprous salts on sulphuric acid. Initial weights: CuCl 0.5119 gram, H_2SO_4 5 cubic centimeters of 0.5 normal acid. Heated at 300° for 1 day; the resulting solution was not noticeably blue, and therefore no significant quantity of cuprous copper could have been oxidized. More or less cuprite formed on the inner glass tube in which the CuCl had been introduced, showing the marked attack that the solution made on the poorer grade of glass. From the fact that no cupric salt was formed it may be concluded that no sulphuric acid was reduced.

Experiment 86.—Similar to experiment 84. Fifteen grams of commercial cuprous chloride was placed in a liter bottle with about 500 grams of copper shot. The bottle was filled with distilled water previously freed from air and shaken about an hour, in order to bring the copper salt into equilibrium with copper, thus making it chiefly cuprous chloride. The precipitate which formed was allowed to settle out. The resulting solution was decanted into another bottle and saturated with hydrogen sulphide. A colloidal suspension of cuprous sulphide resulted which remained suspended indefinitely. When the excess hydrogen sulphide was displaced by passing a stream of carbon dioxide through the solution for an hour, the stability of the suspension was lessened to such an extent that it showed a zone of settling in the course of a few days. When some of the suspension containing carbon dioxide was allowed to flow slowly through a tube filled with coarsely powdered hematite, the resulting solution was entirely clear. It contained principally ferrous bicarbonate, not more than a trace of copper, and no sulphide or sulphate. Indistinct tarnishings on the hematite seemed to resemble chalcopyrite in places and metallic copper in other places, but, as in experiment 84, these products could not be positively identified. The experiment was terminated by stoppage of the tube caused chiefly by coagulation of the suspension.

Experiment 87.—The experiment was started with 2.0 grams of CuCl, and procedure was as in experiment 86. The sulphide was precipitated by exactly 200 cubic centimeters of H_2S gas. The Cu_2S that formed flocculated to such an extent that the solution was not used further.

Experiment 88.—Not completed.

Experiment 89.—Fifteen grams of commercial CuCl was treated as in experiment 86 until the solution was saturated with H_2S. This solution remained in complete suspension for 4 days, when some suspended ferric oxide was mixed with it. The suspended particles began to flocculate at once, and the solution became gradually clear. A few shiny yellow scales resembling chalcopyrite appeared in the precipitate, but these were not separated or positively identified.

Experiment 90.—Some copper wire was heated in a current of dry SO_2 at 500° for half an hour. Scarcely any tarnish appeared on the copper. When the SO_2 was moist, however, the copper was well blackened in half an hour.

Experiment 91.—Action of air on Cu_2S at 500°. A weighed quantity, 0.1000 gram, of Cu_2S gained 0.0469 gram after heating 3 hours at 500°. The product, based on a determination of its content of sulphur, was $CuO.CuSO_4$. Sulphur found, 13.2 per cent as demanded by the written formula. Soluble in dilute HCl.

Experiment 92.—Carbon monoxide and Cu_2S at 500°. Apparently no action.

Experiment 93.—Attempt to prepare colloidal cupric sulphide. A solution containing 1 gram of $CuCl_2.2H_2O$ in 500 cubic centimeters was mixed with a solution of 0.187 gram of Na_2S in 500 cubic centimeters. After 2 days a considerable quantity of black copper sulphide had precipitated, and the solution above was greenish yellow.

Experiment 94.—Similar to experiment 93. Three solutions were prepared, each containing 1 gram of $CuCl_2.2H_2O$ in a liter. Hydrogen sulphide gas was added to each, 38, 76, and 152 cubic centimeters, respectively. Precipitates began to coagulate in all the bottles very soon after the gas was introduced and settled out completely in the course of a few days. The results were not comparable with those in experiment 86.

Experiment 95.—Action of ferric chloride on cuprous sulphide at ordinary temperature. Initial weights: Cu_2S 0.500 gram, $FeCl_3$ 0.0500 gram, HCl 0.005 gram, H_2O 50 cubic centimeters. The air was pumped out of the solution and replaced with carbon dioxide. The first day the yellow color was replaced by a blue-green color. The addition of KSCN gave a red color and a white precipitate, possibly CuSCN. No sulphate had formed. At the end of a week the iron in solution was about 89 per cent in the ferrous state, as shown by titration with $KMnO_4$. After 52 days a similar result was obtained, and still practically no sulphur had gone to the sulphate condition.

Experiment 96.—Ferric oxide and cuprous sulphide. Similar to experiment 9. Weights: Fe_2O_3 0.192 gram, Cu_2S 0.063 gram, H_2SO_4 0.222 gram, H_2O 0.208 cubic centimeter. Heated at various temperatures up to 300°; no copper was observed. The quantity of H_2O was too small to be thoroughly in contact with all the substances.

Experiment 97.—Action of H_2SO_4 on copper. Acid of specific gravity 1.42 developed no visible color on heating a week with copper at 90° C.

Experiment 98.—Action of $FeCl_3$ on Cu_2S. Weights: Cu_2S 0.100 gram, $FeCl_3$ 0.022 gram, H_2O 5.0 cubic centimeters. Heated at 200° for 17 hours; some Fe_2O_3 was deposited in thin flakes, ferrous salt was produced equivalent to 0.0067 gram FeO, also a little SO_4'', and a possible trace of copper. The weakness of this experiment is that the Fe_2O_3 becomes more soluble on cooling, and the ferric salt thus formed would tend to dissolve any copper precipitated, if the Cu_2S did not reduce the ferric salt fast enough.

Experiment 99.—Initial weights: Cu_2S 0.100 gram, $FeCl_3$ 0.022 gram, HCl 0.175 gram, H_2O about 5 cubic centimeters. Heated at 200° for two days; beautiful black crystals formed, probably recrystallized Cu_2S, not more than traces of SO_4'' or sulphur. Ferrous iron in solution equivalent to about 0.006 gram FeO. Cupric and ferric salts present. For repetition see experiment 101.

Experiment 100.—Sulphur and cupric chloride. Initial weights: $CuCl_2.2H_2O$ 0.85 gram, S 0.64 gram, H_2O 5.0 cubic centimeters. On heating at 200° for 17 hours the blue color of the solution had disappeared. After three days' heating there was abundant copper sulphide, blue, lavender, purple, and black.

Experiment 101.—Ferric chloride and cuprous sulphide. Initial weights: Cu_2S 0.240 gram, $FeCl_3$ 0.325 gram, HCl 0.200 gram, H_2O to a volume of 5 cubic centimeters. The yellow color began to change to green immediately on mixing, and on warming to 90° sulphur appeared in the course of an hour. Heated at 200° for two days; the solution was still slightly yellow, the solid somewhat purple and blue, suggesting covellite. After the solution was heated four days more there was no further visible change except an increase in the quantity of covellite. Analysis then showed in the precipitate Cu 0.0946 gram, S 0.0343 gram, and, in the solution, SO_4'' 0.0378 gram. The results can not be reconciled with any simple single reaction. It is believed that all the following reactions occurred either simultaneously or in succession.

$$Cu_2S+4FeCl_3=4FeCl_2+2CuCl_2+S \qquad (44)$$

$$Cu_2S+2FeCl_3=CuCl_2+2FeCl_2+CuS \qquad (43)$$

$$4S+4H_2O=3H_2S+H_2SO_4 \qquad (10)$$

$$CuCl_2+H_2S=CuS+2HCl \qquad (67)$$

Or, by combining (44), (10), and (67) to eliminate sulphur one obtains

$$4Cu_2S+16FeCl_3+4H_2O=16FeCl_2+5CuCl_2+H_2SO_4+3CuS+6HCl \qquad (68)$$

Analysis of the products seems to show that about half of the precipitate was unchanged Cu_2S, so that on this basis 0.175 of the original Cu_2S reacted. The requirements of equation (68) are then as follows:

Quantities required for equation (68) and quantities found

	Calculated	Found
	Gram	*Gram*
Cu as CuS	0.053	0.043
S as CuS	.026	.021
SO_4'' in solution	.026	.038

These results indicate that another reaction must have taken place to a small extent, forming H_2SO_4 without the simultaneous production of CuS. This reaction was probably some such reaction as the following:

$$Cu_2S+10FeCl_3+4H_2O=2CuCl_2+10FeCl_2+H_2SO_4+6HCl \qquad (69)$$

Adding equations (68) and (69) we obtain (quite arbitrarily)

$$5Cu_2S+26FeCl_3+8H_2O=26FeCl_2+7CuCl_2+2H_2SO_4+3CuS+12HCl \qquad (70)$$

Assuming that 0.175 gram of Cu_2S reacted we have by equation (70) the quantities shown in the following table:

Quantities required for equation (70) and quantities found

	Calculated	Found
	Gram	*Gram*
Cu as CuS	0.042	0.043
S as CuS	.021	.021
SO_4'' in solution	.042	.038

Apparently the net result is approximately a combination of equations (68) and (69).

Experiment 102.—Action of Cu_2S in excess on $FeCl_3$. Initial weights: Cu_2S 0.300 gram, $FeCl_3$ 0.150 gram=1.41 cubic centimeters of stock solution, HCl 0.195=1 cubic centimeter of stock solution, H_2O in addition 2.5 cubic centimeters. Heated at 200° for 1 day. Some covellite was formed, also cuprous chloride, which separated on cooling. The solution was still very pale yellow. Probable reaction:

$$Cu_2S+FeCl_3=FeCl_2+CuCl+CuS \qquad (45)$$

Heated 5 days longer at 200°. The covellite became gradually less noticeable. The yellow element in the color of the solution did not seem to disappear entirely. Final result: Total sulphur in precipitate, 0.0592 gram (taken as Cu_2S 0.0603 gram); SO_4'' in solution 0.0033 gram.

Experiment 103.—Initial weights: Cu_2S 0.16 gram, CuCl 0.50 gram, $CuCl_2$ 0.12 gram, $FeCl_2$ 0.033 gram, HCl 0.39 gram, H_2O about 4.0 cubic centimeters. Heated at 150° for 1 day and at 200° for 1 day; no visible changes. When heated at 250° the tube exploded.

Experiment 104.—Copper and sulphuric acid. Initial weights: Cu 0.5 gram, H_2SO_4 0.50 gram, H_2O 2.85 cubic centimeters. Volume of tube 12 cubic centimeters. Heated at 250° for 3 days. Some of the copper recrystallized on cooling; in fact, only a little of the original wire remained. Cu_2S and $CuSO_4$ were formed. Heated 2 days more; the copper mostly recrystallized on cooling. Analysis of products is given in Tables 9 and 10. From later work discussed on pages 15 and 37 it is inferred that theoretically all the copper taken in this experiment should have dissolved at 250°—that is, if the sulphuric acid was not too greatly reduced by the reaction to be effective.

Experiment 105.—Effect of Cu_2O. Initial weights: Cu_2S 0.16 gram, Cu_2O 0.429 gram, H_2O 5.0 cubic centimeters. Heated at different temperatures, finally 2 days at 250°; no visible copper.

Experiment 106.—Same as experiment 105 with 0.05 Fe_2O_3 in addition. Heated finally 4 days at 250°; no visible copper.

Experiment 107.—Cu_2S and $Fe_2(SO_4)_3$. Weights: Cu_2S 0.30 gram, $Fe_2(So_4)_3$ 0.192 gram, H_2SO_4 0.513 gram, H_2O 5.0 cubic centimeters. Heated at 150° for 2 days; no visible change except that the solution turned blue. Heated at 250° for 2 days; no copper deposited on cooling.

Experiment 108.—Cuprous sulphide, cupric sulphate, and cuprous oxide. Initial weights: Cu_2S 0.08 gram, $CuSO_4.5H_2O$ 0.38 gram, Cu_2O 0.28 gram, H_2O 5 cubic centimeters. Heated at 200° for 1 day; a little copper formed, solution still blue. Heated another day; a little bright-green basic salt formed. The precipitate was now analyzed. Sulphur found 0.0151 gram, originally taken as cuprous sulphide 0.0160 gram, which shows that a little of the sulphur of the cuprous sulphide had been oxidized.

The experiment was repeated, using Cu_2S 0.106 gram, $CuSO_4.5H_2O$ 0.50 gram; otherwise as above. Heated to 300° for 4 days. A little copper and a green basic salt were formed. Both Cu_2S and Cu_2O remained. The solution was moderately blue. Two years later no basic salt was visible; Cu_2S, Cu, and Cu_2O remained.

Experiment 109.—Cupric chloride and cuprous sulphide. Initial weights: Cu_2S 0.08 gram, $CuCl_2.2H_2O$ 0.26 gram, H_2O 5.0 cubic centimeters. Heated at 200° for 1 day; found in solution as sulphate 0.0027 gram=0.0080 SO_4''. About 17 per cent of the sulphur in the chalcocite was oxidized by heating at 200° for 1 day. Cuprous chloride was suspected as another product of the reaction. (See further experiment 131.)

Experiment 110.—Oxidation of chalcocite by cupric sulphate. Initial weights: Cu_2S 0.08 gram, $CuSO_4.5H_2O$ 0.375 gram, H_2O 5.0 cubic centimeters. Heated at 200° for 1 day; a very little copper formed, also a green basic salt. Heated 1 day more. Analyzed. Found 0.0160 gram of sulphur in precipitate, identical with sulphur taken as Cu_2S. Practically no acid in the solution. The reaction had scarcely started.

Experiment 111.—Cuprous sulphide, cupric sulphate, and sodium acetate. Initial weights: Cu_2S 0.08 gram, $CuSO_4.5H_2O$ 0.50 gram, $NaC_2H_3O_2.3H_2O$ 0.72 gram. Heated for 2 days at 200°; a little copper was formed and a large quantity of a red salt which was not determined. The blue color of the solution practically disappeared.

Experiment 112.—Oxidation of Cu_2S at 200°. (See Table 8.) Four days' heating at 200° gave a bare trace of copper on cooling.

Experiment 112.—Oxidation of Cu_2S at 200°. (See Table 8.) Four days' end. Weights as given in Table 8; the solution was dilute. Heated for 6 days with one end in furnace supposed to yield 250°, the other end water-cooled. No copper. The acidity was unchanged. Evidently the reaction did not progress appreciably, probably because 250° was not attained.

Experiment 114.—Similar to experiment 62, but more $CuSO_4$ was taken. Weights in Table 8. Heated at 250° for two days. A measurable quantity of copper deposited on cooling. Results of analyses in Tables 9 and 12.

Experiment 115a.—Tube broke.

Experiments 115b and 115c.—Heated at 300° for four days and six days respectively. Weights and analyses shown in Tables 8–12. Experiments at temperatures above 250° were made by inclosing the tubes in an iron bomb with water inside to equalize the pressure on the tubes.

Experiment 116.—Similar to experiments 115*b* and 115*c*; heated 56 days at 250°. (See Tables 8–12.)

Experiment 117.—Effect of $FeSO_4$. (See Tables 8–12.)

Experiment 118.—Run in a silica tube. Initial weights: Cu_2S 0.32 gram, $CuSO_4.5H_2O$ 1.500 grams, H_2SO_4 0.10 gram, H_2O 4.96 centimeters. Heated 11 days at 350°; a little copper appeared on cooling. Not analyzed.

Experiment 119.—Ferric oxide, cuprous sulphide, etc. (See Tables 8–12.) Heated at 300° for 6 days. A little copper was deposited on cooling, and the solution was slightly blue.

Experiment 120a.—Action of sulphuric acid on Jena glass tubes. Exactly 5 cubic centimeters of 0.5 normal sulphuric acid was placed in a Jena glass tube, 22 centimeters long, 1 centimeter in internal diameter, and heated in a horizontal position at 200° C. for 20 days. Original H_2SO_4 0.1225 gram, remaining 0.0932 gram, neutralized 0.0293 gram. Some crystals formed on the inside of the tube which qualitative tests indicated to consist of SiO_2, SO_4'', Ca, and possibly K. There was not enough material to analyze. E. S. Larsen examined it microscopically and thought that three separate things were present; some basal hexagonal tablets, uniaxial $(+)\omega=1.58$ and ϵ about 1.60, possibly an alunite; some skeletal prisms with n about 1.47; and some needles with high index of refraction. Some of the crystals formed little radiating clusters, and some grew along the glass. The solution was found to contain SiO_2 0.0192 gram, Al_2O_3 0.0010 gram, CaO 0.0055 gram, MgO trace, K_2O trace, Na_2O not determined.

Experiment 120b.—Similar to preceding, in a tube 16 centimeters long, heated 11 days at 300°. Original H_2SO_4 0.1225 gram, remaining 0.1125 gram, neutralized 0.0100 gram, which is less than found in 120*a*. No crystals formed in the tube. The solution gave SiO_2 0.0067 gram, CaO 0.0010 gram, MgO trace, K_2O 0.0036 gram, Na_2O not determined.

Experiment 121.—Ferric sulphate and cupric sulphide. Resembled experiment 107. Initial weights and results shown in Table 8. Heated for 18 days at 200°; solution slightly blue but no copper. Heated 11 days more at 300°; some copper appeared on cooling. The sulphur of the solids was more than enough to form Cu_2S, so that either sulphur or CuS may also have been present.

Experiment 122.—Resembled experiment 118. A silica tube of volume about 15 cubic centimeters was used. (See Tables 8–12.) No acid was used; that formed in the reaction prevented any formation of basic salt, even at 300°.

Experiment 123.—Similar to experiment 122 but with H_2SO_4 present, also less $CuSO_4$. The copper deposited on cooling was only about half that formed in experiment 123. (See Tables 8–12.)

Experiment 124.—Action of cupric sulphate on sulphur dioxide. Initial weights: $CuSO_4.5H_2O$ 2.00 grams, SO_2 0.222 gram, H_2SO_4 0.49 gram, H_2O 10.0 cubic centimeters. Heated at 250° for 1 day; apparently nothing but copper was formed. Heated 4 days more; in addition to the copper a trace of fine dark crystals, apparently either CuS or Cu_2S, was formed.

Experiment 125.—Resembled experiment 114 but with more $CuSO_4$. Some of the $CuSO_4$ crystallized out on cooling. Details in Tables 8–12.

Experiment 126.—Resembled experiment 69. Initial weights: Cu_2S 0.10 gram, CuCl 0.20 gram, Cu 0.10 gram, HCl 0.20 gram, H_2O 5.0 cubic centimeters. Heated 2 days at 200°; the CuCl recrystallized on cooling. Heated 5 days at 250°; a very little copper was recrystallized and deposited as a red tint on some of the CuCl on cooling, especially at a certain zone near the end of the tube. No sulphate was formed.

Experiment 127.—Similar to experiment 122 but heated at 350°. Details in Tables 8–12. Silica tube.

Experiment 128.—Resembled experiment 49. Initial weights: Cu 0.50 gram, H_2SO_4 0.50 gram, H_2O 2.85 cubic centimeters. Heated 4 days at 350°; considerable Cu_2S was formed. Some copper was recrystallized, but the results resembled in most respects those obtained by starting with Cu_2S and $CuSO_4$. The acid was not all used up, but the copper may not have been present in sufficient amount. Details in Tables 8–12.

Experiment 129.—Neutralizing action of rock from the Leucite Hills, Wyo., supposed to be wyomingite, on sulphuric acid. Initial weights: Wyomingite 1.0 gram, HCl 0.5 gram, H_2O 5.5 cubic centimeters. Heated 2 days at 250°; HCl then 0.150 gram; neutralized 0.350 gram. Potassium in solution as K_2O, 0.120 gram=12 per cent of rock. The alkalies were apparently all dissolved. In fact, a little potassium may have dissolved from the tube, or the rock may have been orendite with approximately 12 per cent K_2O.

Experiment 130.—Neutralizing action of Jena combustion tubing, powdered and selected between 60 and 200 mesh. Quantity taken, 1.0 gram; H_2SO_4 0.100 gram, H_2O 6.96 cubic centimeters. Heated 2 days at 250°. H_2SO_4 was then 0.0684 gram; neutralized 0.032 gram.

Experiment 131.—Oxidizing action of cupric salts. Initial weights: Cu_2S 0.16 gram, $CuCl_2$ 0.96 gram, H_2O 5.60 cubic centimeters. Heated 2 days at 250°; the sulphur of the Cu_2S was completely oxidized to sulphate. A considerable quantity of CuCl crystallized out on cooling. The solution was a pale willow-yellow.

Experiment 132a.—Resembled experiment 49. Initial weights: Cu 0.50 gram, H_2SO_4 0.1225 gram, H_2O 4.96 cubic centimeters. Heated 4 days at 250°. The resulting solution was pale blue. A small quantity of copper was recrystallized and a trace of Cu_2S formed. The recrystallized copper, separated as well as possible, after correction for a trace of sulphide, was found to be 0.0050 gram. Copper in solution 0.0069 gram. The solution was boiled and a very small amount of SO_2, 0.008 gram, found by collecting in $KMnO_4$.

Experiment 132b.—A duplicate of the tube analyzed in 132a was heated 4 days more at 300°. Found: In the solid, copper 0.473 gram, sulphur 0.0065 gram, equivalent to 0.0323 gram Cu_2S; in the solution, Cu 0.0225 gram, SO_4'' 0.1005 gram, acidity by titration equivalent to 0.078 gram H_2SO_4. The results of calculation of the possible reaction, given in Table 12, do not conform very closely to the requirements of equation (17), which is the reverse of equation (36) expressing the action of cupric sulphate on chalcocite.

Experiment 133.—Similar to preceding experiment. Initial weights: Cu 0.127 gram, H_2SO_4 0.392 gram, H_2O 0.392 cubic centimeter. Volume of tube 14 cubic centimeters. Heated at 300° for 4 days; the copper was entirely recrystallized with the production of Cu_2S and $CuSO_4$. In fact, the solution nearly all crystallized as $CuSO_4.5H_2O$. The products were not analyzed.

Experiment 134.—Similar to preceding experiment. Initial weights: Cu_2S 0.160 gram, H_2SO_4 0.196 gram, H_2O 7.93 cubic centimeters in all. Heated at 300° for 4 days; there was no visible change. On opening the tube no SO_2 could be detected by the smell, but on boiling the solution, absorbing the gas in water, and titrating with $KMnO_4$, a possible trace of SO_2 was indicated.

Experiment 135a.—Effect of the presence of CuCl on reaction (36). Initial weights: Cu_2S 0.16 gram, $CuSO_4$ 1.21 grams, CuCl 0.40 gram, introduced dry in separate inner tube, H_2O 5.0 gram. Heated at 300° for 4 days. The tube was considerably attacked. A bright-green salt was formed and possibly Cu_2O but no copper.

Experiment 135b.—Initial weights: Cu_2S 0.32 gram, $CuSO_4$ 1.21 gram, CuCl 0.1996 gram, H_2SO_4 0.1225 gram, H_2O 4.96 cubic centimeters. Heated at 300° for 2 days. Some of the green salt formed, also very good crystals of Cu_2O, especially on the poorer glass of the inner tube, but only one or two small flakes of copper.

Experiment 136.—To see if the copper is formed by reaction (36) at the high temperature. Initial weights: Cu_2S 0.32 gram, $CuSO_4.5H_2O$ 3.00 grams, H_2O 5.0 cubic centimeters. Heated at 250° for 15 hours and inspected while hot. The color was a dark green with a large quantity of basic salt, but no copper was visible. When heated 2 days more the quantity of basic salt had decreased, but no copper appeared. When heated 3 days more the basic salt was mostly gone. When heated 2 days more the solution was green, but no copper appeared. The tube was now allowed to cool in a sloping position. Crystals of copper appeared in the solution, which became blue. A little $CuSO_4.5H_2O$ crystallized, also a little green basic salt and a few octahedra of cuprite.

Experiment 137.—Similar to experiment 49. Initial weights: Copper 1.0003 grams, H_2SO_4 0.3691 gram, H_2O 4.88 cubic centimeters. Heated at 200° for 2 days; no visible color developed, but a trace of Cu_2S formed. When heated at 250° for 7 hours more a pale-yellowish color developed, with considerable Cu_2S. When heated 17 hours more the solution was faintly blue, and a few specks of recrystallized copper appeared in the end of the tube, which was probably the coldest part; this shows how easily the copper migrates from warm to cold regions. When heated 1 day more the solution was a pale greenish blue. On cooling the solution deposited a lot of copper and became blue. Most of the Cu_2S was well crystallized, showing lathlike and feathery forms.

Experiment 138.—Similar to experiments 49 and 132 but heated at 300°. Initial weights: Copper 1.00 gram, H_2SO_4 0.3691 gram, H_2O 4.88 cubic centimeters. Heated at 300° for 2 days and cooled. Tube now contained Cu_2S, recrystallized copper, and $CuSO_4$, estimated colorimetrically at 0.086 gram copper. Analysis: Copper recrystallized, corrected for Cu_2S, 0.0794 gram. Total copper in solid 0.9054 gram; total sulphur 0.0150 gram. Solution: Copper 0.0896 gram, SO_4'' 0.3180 gram. The calculations based on these determinations are given in Tables 1 and 11.

Experiment 139.—Similar to experiment 138 but heated at 350° in silica tube. Duplicates, one in silica, one in glass. The glass tube was much attacked but held. Weights: Copper 1.000 gram, H_2SO_4 0.3691 gram, H_2O 4.880 cubic centimeters. Heated at 350° for 2 days. The contents of the silica tube were analyzed. Solid: Recrystallized copper, corrected for Cu_2S, 0.0996 gram, total copper 0.8704 gram, total sulphur 0.0212 gram. Solution: Copper 0.1246 gram, SO_4'' 0.3005 gram. For calculations see Table 1.

Experiment 140.—Pyrite and copper in the presence of water. Uncompleted.

Experiment 141a.—Effect of high alkalinity. Weights: Fe_2O_3 0.768 gram, Cu_2S 0.064 gram, NaOH 5 cubic centimeters of solution of specific gravity 1.19. Heated at 200° for 3 hours; no visible changes occurred.

Experiment 141b.—Similar to experiment 141*a*. Weights: Fe_2O_3 0.764 gram, Cu_2S 0.064 gram, NaOH 5 cubic centimeters of solution 15.5 normal. Heated at 300° for 1 day. The tube cracked and was very much attacked, so that the results were not satisfactory. However, there were no evidences of copper or ferrous sulphate. Only on extracting with dilute acid was ferrous iron found, and this is explicable by the evidence of experiment 38.

Experiment 142.—Pyrrhotite and ferric oxide. Weights: FeS 0.088 gram, Fe_2O_3 0.64 gram, H_2O 5.0 cubic centimeters. Heated at 300° for 1 day; no soluble SO_4'' or Fe'' was formed. Hydrochloric acid of course gave some Fe'', but no SO_4'' in the solid.

Experiment 143.—Ferric oxide and sodium sulphide. Initial weights: $FeCl_3$ equivalent to 0.897 gram Fe_2O_3, NaOH 1.88 gram=2.17 cubic centimeters of 15.5 normal NaOH, Na_2S 0.78 gram=1 cubic centimeter of 2 normal Na_2S. Heated at 300° for 1 day. Some FeS was formed at once. The tube was much attacked. The inside of the tube was more or less covered by a greenish coating. No soluble SO_4'' or Fe'' found; in fact, the solution was faintly alkaline. The solution gave a white precipitate on acidifying with H_2SO_4 and consumed a small amount of $KMnO_4$ equivalent to 0.0034 gram FeO. No pyrite could be detected. The dry powder was slightly magnetic.

Experiment 144.—Ferric oxide and sulphur. Compare experiment 24. Weights: Fe_2O_3 0.500 gram, sulphur 0.05 gram, H_2O 5.0 cubic centimeters. Heated at 300° for 1 day; the solution contained considerable SO_4'' (not acid, hence probably K_2SO_4 from the glass) and a little Fe''. The solid appeared to contain some sulphide, perhaps FeS or FeS_2 in the form of a slimy dull-gray powder not rapidly soluble in acid but of indistinct character under the microscope. Hydrochloric acid dissolved some ferrous compound, at least 0.0034 gram FeO. No residual sulphur could be detected.

Experiment 145.—Ferric oxide and cuprous chloride in acid solution. Weights: $Fe_2(SO_4)_3$ and H_2SO_4=0.0765 gram Fe_2O_3 and 0.1535 gram H_2SO_4 in 1 cubic centimeter of solution, H_2O 2.0 cubic centimeters, CuCl 0.3015 gram (in an inner capsule). The substances were not mixed until the air was very thoroughly pumped out and the tube sealed. After mixing the solution soon developed a blue color, estimated colorimetrically to be equivalent to 0.056 gram of cupric copper. Theory for complete reduction of the ferric salt 0.061 gram. Heated at 125° for 2 days; some Fe_2O_3 and possibly other hydrolytic products were deposited, and the solution became somewhat paler.

Experiment 146.—A blank test on the CuCl, treated as in the preceding experiment but without any ferric salt, gave no blue color. After heating at 125° for 2 days and cooling a very little copper deposited on cooling. No blue color was visible.

Experiment 147.—Gradual neutralization of a ferrous-cupric solution likely to deposit copper. Weights: H_2O 50 cubic centimeters, $FeSO_4.7H_2O$ 0.0278 gram, $CuSO_4.5H_2O$ 0.250 gram, $NaC_2H_3O_2.3H_2O$ 1.09 grams. The material was sealed in a vacuum, the solids being in a separate tube. Mixed. A fine yellow precipitate soon began to form and in 15 minutes had flocculated. The solution was then somewhat greenish, and the precipitate gradually became the color of ferric hydroxide, verging slightly toward yellow. Heated at 100° for 4 hours and then cooled; the precipitate was decidedly red, although no particles of copper could be identified by any metallic appearance. The solution was nearly colorless, but after filtering off the precipitate in air it gave only 0.0050 gram iron and 0.0050 gram copper. When the solid was immersed in silver sulphate solution metallic silver was precipitated, but as cuprous oxide gives the same result this does not prove that metallic copper existed in the precipitate, and there is no evidence that it was present. The fact that ferric hydroxide appeared to be formed and that the precipitate reduced silver sulphate solution seems to show that the precipitate was a mixture of ferric and cuprous oxides or hydroxides.

Experiment 148.—Similar to experiment 147, but with twice as much ferrous sulphate and sodium acetate. The precipitate did not coagulate as quickly as that in experiment 147. The flask was heated very gradually up to 100° over the course of a week. The results were similar to those obtained in experiment 147 except that the color of the precipitate was much more yellow, hardly at all red, resembling freshly precipitated cuprous oxide. The solution gave 0.0062 gram iron and 0.0018 gram copper.

Experiments 149–153.—Solubility of CuCl in solutions of $CaCl_2$ at 25° C. The determinations were made in an atmosphere of nitrogen in the apparatus shown in Figure 2. It will readily be seen that water or calcium chloride solution could be freed from air and introduced into the tube or the saturated solution removed from it by connecting as desired, turning the proper stopcocks, and allowing nitrogen from a cylinder of the compressed gas to pass as slowly or fast as desired. The precipitated CuCl was first well washed. The tube containing the mixture was then shaken from time to time and kept at constant temperature in the thermostat accurate to 0.1°. After settling, the clear solutions were decanted into a graduated cylinder and weighed. They were then analyzed by separating the copper as sulphide and determining it by electrolysis. The calcium was precipitated as oxalate and weighed as lime. The results are shown in Table 13.

Experiment 155.—This experiment was similar to experiment 14. Initial weights: $FeSO_4.7H_2O$ 0.5 gram, $CuSO_4.5H_2O$ 0.5 gram, H_2O 5.0 cubic centimeters. The tube was observed from time to time during 24 hours while it was being heated at 200°. No copper appeared, but some red substance, thought possibly to be cuprite, was formed. Copper appeared on cooling, however, but redissolved on heating. The experiment shows that the copper obtained in Stokes's experiment was probably precipitated by cooling and not by reaction at a high temperature.

Experiment 157.—This experiment was performed to neutralize the acidity gradually and thus to increase the quantity of Cu_2SO_4 formed. Initial weights: $FeSO_4.7H_2O$ 0.5 gram, $CuSO_4.5H_2O$ 0.5 gram, wyomingite 0.2 gram, H_2O 5.0 cubic centimeters. After heating the tube at 200° for two days no copper was visible in the hot solution. The tube was then tilted and cooled slowly. When cold a considerable quantity of copper had separated from the solution, and no significant quantity of it could be seen in the solids, showing that the copper is not formed while hot, at least for a certain initial period.

Experiment 158.—Initial weights: $FeSO_4.7H_2O$ 0.5 gram, $CuSO_4.5H_2O$ 0.5 gram, Cu_2O 0.8 gram, H_2O 5.0 cubic centimeters. The tube after heating at 200° for two days showed no copper while hot, but after tilting the tube and cooling as in the previous experiment copper was observed in the solution and only a very few specks in the solid. Some feathery crystals were also present in the solution, but not definitely shown to be Cu_2SO_4. There was not as much hematite in the solid as in the preceding experiment.

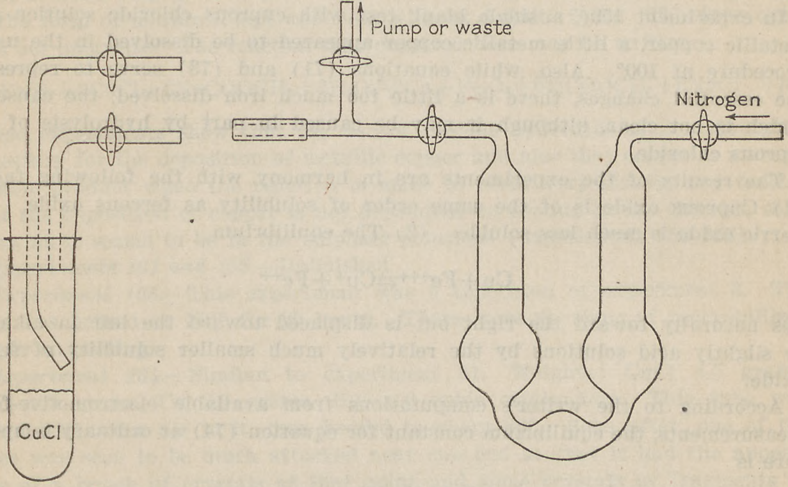

FIGURE 2.—Apparatus used in experiments 149–153

Experiments 159a–159g.—Reaction of CuCl on FeO at 100°. A ferrous chloride solution was made by immersing an excess of iron in hydrochloric acid, the solution being protected by an atmosphere of nitrogen. This solution was withdrawn quantitatively as desired and precipitated by an exact equivalent of caustic soda solution, also in an atmosphere of nitrogen. In most of the experiments saturated sodium chloride was used as a diluent to the extent of half the volume of the main solution. Similarly, cuprous chloride dissolved in a concentrated solution of sodium chloride was added to the suspension of ferrous oxide. All reactions were done at about 100° C. in a closed flask, the contents of which could be boiled in a slow stream of nitrogen. In experiment 159*c* the sodium hydroxide was added to the mixed ferrous and cuprous salts instead of first precipitating the ferrous oxide. The data obtained are given in Table 14, in which the lines entered as "theory" are computed from the weights of FeO or CuCl taken, depending on which was in excess, according to equations (71), (72), and (73).

$$3FeO+2CuCl=2Cu+Fe_2O_3+FeCl_2 \qquad (71)$$

$$FeO+2CuCl=Cu_2O+FeCl_2 \qquad (72)$$

$$4FeO+2CuCl=2Cu+Fe_3O_4+FeCl_2 \qquad (73)$$

The precipitate formed in these experiments, after drying on filter paper in air, was strongly magnetic. This suggests that magnetite was one of the products, as indicated by equation (73).

The data in Table 14 show that equation (72) may be left out of consideration. Equation (71) evidently expresses the principal change, especially when CuCl is in large excess. At the same time, however, some magnetite appears to be formed, as expressed by equation (73), and this equation appears to be still better verified as the excess of CuCl is decreased, as would be expected.

In experiment 159*f*, a single blank test with cuprous chloride solution and metallic copper, a little metallic copper appeared to be dissolved in the usual procedure at 100°. Also, while equations (71) and (73) serve to represent the essential changes, there is a little too much iron dissolved, the cause of which is not clear, although it may be caused in part by hydrolysis of the cuprous chloride.

The results of the experiments are in harmony with the following facts: (1) Cuprous oxide is of the same order of solubility as ferrous oxide. (2) Ferric oxide is much less soluble. (3) The equilibrium

$$Cu+Fe^{+++}\rightleftarrows Cu^{+}+Fe^{++} \qquad (74)$$

lies naturally toward the right but is displaced toward the left in alkaline or slightly acid solutions by the relatively much smaller solubility of ferric oxide.

According to the writer's computations from available electromotive-force measurements, the equilibrium constant for equation (74) at ordinary temperature is

$$\frac{[Cu^{+}]\ [Fe^{++}]}{[Fe^{+++}]}=5{,}000 \qquad (75)$$

If the solubility products of $Fe(OH)_2$, $Fe(OH)_3$, and CuOH at 25° are taken as 19.8×10^{-15}, 1.1×10^{-36} and 1.6×10^{-9} respectively, it is easily calculated that in solution as alkaline as $Fe(OH)_2$ itself ferrous oxide should readily convert cuprous salts into metallic copper. As a matter of fact, however, ferrous chloride is formed, and this is even more favorable for the precipitation of copper. The final solution in experiment 159*g*, for example, contained ferrous chloride, 0.0042 molal, and cuprous chloride dissolved in sodium chloride, 0.0281 molal. The unknown ionic concentrations are $[Cu^{+}]$ and $[Fe^{+++}]$, the first depending on the existence of a complex ion and the second depending on $[OH^{-}]$—that is, on the hydrogen ion concentration or pH value, and possibly on the existence of magnetite as a solid phase.

According to Bodländer and Storbeck[73] $[Cu^{+}]$ will be highest in the least saline solutions. Evidently, however, $[Fe^{++}]$ can be varied more widely than $[Cu^{+}]$.

---

[73] Bodländer, G., and Storbeck, O., Beiträge zur Kenntnis der Cuproverbindungen: Zeitschr. anorg. Chemie, vol. 31, pp. 1–41, 458–476, 1902.

Experiments 160a–160j.—Action of $FeCl_2$ on CuCl in solutions of regulated pH, or hydrogen ion concentration. The pH value was fixed by different proportions of acetic acid and sodium acetate. When ferrous chloride and cuprous chloride were introducted into such solutions, boiling in an atmosphere of nitrogen, no copper was precipitated if the pH value was initially less than obout 5.0. Under certain conditions, shown more fully in Table 15, with a pH value of 5.2 a slight film, probably containing some copper, formed on the walls of the flask in the course of 2 hours boiling. The experiment was repeated with less sodium chloride present, but no crystals of copper could be detected. With a pH value of 5.38 and somewhat more sodium chloride, the deposit showed some small particles of ferric oxide, each surrounding a nucleus of minute crystals of copper visible with a lens.

Repetition of the experiment with more ferrous chloride and less cuprous chloride, in a flask that had a slight film remaining from the previous experiment, gave a deposit that showed under a lens or a microscope numerous crystals of copper, some spicules, some thick crystals showing triangular faces, most of them largely covered with iron oxide, which also adhered to the glass in the form of minute lumps and flocs without definite form. This iron oxide was not magnetic. The reaction that occurred here may be written

$$2FeCl_2+2CuCl+6NaCOOCH_3+3H_2O=2Cu+Fe_2O_3+6HCOOCH_3+6NaCl \quad (76)$$

These experiments show that the use of ferrous hydroxide is not absolutely necessary for the deposition of metallic copper and also that copper is a recognizable product when the reaction is made to occur very slowly, and further that the deposition of copper is not dependent on cooling in the chloride solutions, as it seems to be in the sulphate solutions (experiments 155–158).

Experiments 161 and 162.—Unfinished.

Experiment 163.—This experiment was a repetition of experiment 3. The tube was heated at 150° for 25 hours. There were no signs of recrystallized copper on cooling.

Experiment 164.—Similar to experiment 31. Weights: CuCl 4.5 grams, NaCl 3.5 grams, Cu 2.0 grams, H_2O 6.0 cubic centimeters. This tube was sealed with some air in it, then heated to about 80°. Soon after, one of the wires was seen to be much attacked near one end so that it had the appearance of a bunch of crystals at that point and some crystals or fragments of copper were loose in the tube. It would therefore have been impossible to note any recrystallization of copper in this tube. When the tube was heated at 150° for 15 hours a little green basic salt formed, and much of the CuCl recrystallized on cooling. When the tube was heated at 175° for 5 hours and tilted while hot the green basic salt remained with the copper and had therefore not dissolved in the hot solution, but most of the CuCl had dissolved and recrystallized on cooling.

Experiment 165.—Similar to experiment 164, but 4.0 cubic centimeters of H_2O and 2 cubic centimeters of concentrated HCl were taken instead of 6 cubic centimeters of H_2O. When the tube was heated at 150° for 15 hours no recrystallized copper was observed on cooling. The solution was practically colorless. The tube was heated at 175° for 5 hours and tilted hot; about 95 per cent of the CuCl recrystallized, showing a solubility of approximately 700 grams of CuCl per liter in this solution at 175° C. No basic salt was formed. The CuCl was beautifully crystallized.

TABLE 8.—*Substances taken and conditions of experiment*

[All weights in grams]

Experiment No.	Temperature (°C.)	Duration of experiment (days)	$CuSO_4$	Cu_2S	H_2SO_4	$FeSO_4$	Fe_2O_3	H_2O
[a] 15	200	2	--------	0.02	0.06	0.50	0.08	5.0
[a] 62	230	3	0.320	.08	.23	--------	--------	5.35
[b] 64	200	2	.320	.08	.69	--------	--------	5.69
[b] 65	200	1	.320	.08	None.	[c] 4.0	--------	5.2
[a] 66	200	6	.160	.08	None.	--------	--------	5.09
[a] 67	200	9	.320	.08	.10	--------	--------	5.26
[b] 72	200	6	--------	.02	--------	.273	--------	4.8
[b] 77	200	3	--------	.02	[d] .024	--------	.04	5.0
[b] 78	200	3	--------	.02	[d] .040	.50	.130	5.23
[b] 101	200	6	--------	.24	[e] .201	--------	[f] .325	2.0
[b] 102	200	6	--------	.30	[e] .195	--------	[f] .150	3.5
[a] 108	200	2	.243	.08	[g] .28	--------	--------	5.14
[b] 109	200	1	[h] .26	.08	--------	--------	--------	5.08
[a] 110	200	2	.24	.08	--------	--------	--------	5.13
[a] 112	200	4	.24	.08	.23	--------	--------	20.3
[b] 113	200	6	.24	.08	.23	--------	--------	30.3
[i] 114	250	2	1.919	.1600	.340	None.	None.	8.25
115*b*	300	4	1.919	.1600	.340	None.	None.	8.25
115*c*	300	10	1.919	.1600	.340	None.	None.	8.25
116	250	56	1.919	.1600	.340	None.	None.	8.25
117	250	8	.640	.1278	.340	.546	None.	6.06
119	300	6	None.	.1000	.444	None.	.192	5.00
120*a*	200	16	None.	None.	.1225	None.	None.	5.35
120*b*	300	11	None.	None.	.1225	None.	None.	5.35
121	300	11	None.	.1000	.742	None.	[j] .192	5.21
122	300	11	1.215	.3200	None.	None.	None.	5.69
123	300	11	.92	.32	.70	None.	None.	5.26
125	300	4	3.84	.500	.340	None.	None.	5.00
127	350	4	1.21	.16	None.	None.	None.	5.69
128	350	4	[k] .50	None.	.500	None.	None.	2.85
132*a*	250	4	[k] .50	None.	.1225	None.	None.	4.96
132*b*	300	4+	[k] .50	None.	.1225	None.	None.	4.96
138	300	2	[k] 1.00	None.	.3691	None.	None.	4.88
139	350	2	[k] 1.00	None.	.3691	None.	None.	4.88

[a] A trace of copper formed.
[b] No copper observed.
[c] $CaCl_2$.
[d] SO_2.
[e] HCl.
[f] $FeCl_3$.
[g] Cu_2O.
[h] $CuCl_2 \cdot 2H_2O$.
[i] Measurable copper formed in most of the succeeding experiments.
[j] $Fe_2(SO_4)_3$.
[k] Metallic copper.

TABLE 9.—*Analysis of solid residues*

[All weights in grams]

Experiment No.	Temperature (°C.)	Duration of experiment (days)	Total copper	Sulphur	Copper equivalent to sulphur	Metallic copper
62	220	6	0.0659	----------	----------	A little.
101	200	6	.0946	0.0343	0.1360	----------
102	200	6	----------	.0592	.2347	----------
104	250	5	.1461	.022	.0872	0.0589
108	200	2	----------	.0151	.0600	Trace.
110	200	2	----------	.0160	----------	Trace.
112	200	4	----------	----------	----------	Trace.
114	250	2	.1422	.0211	.0838	.0584
115*b*	200	4	.1977	.0225	.0894	.1083
115*c*	200	10	.2120	.0157	.0623	.1497
116	250	56	.1695	.0260	.1031	.0664
117	250	8	.1372	.0255	.1014	.0358
119	300	6	.0530	.0101	.0402	.0128
121	300	11	.0500	.0143	----------	Present.
122	300	11	.3405	.054	.214	.126
123	300	11	.276	.0515	.208	.068
125	300	4	.5033	.626	.248	.255
127	350	4	.2590	.0087	.035	.224
128	350	4	.2920	.0347	.1376	[a] .1544
132*a*	250	4	[b] .0067	.0004	.0017	[c] .0050
132*b*	300	4	.473	.0065	.0258	.0447
138	300	2	.9054	.0147	.0582	.847

[a] 0.3456 reacted.

[b] Copper recrystallized with a little sulphide.

[c] Copper recrystallized.

TABLE 10.—*Analysis of solutions*

[All weights in grams]

Experiment No.	Copper	Total SO_4''	H_2SO_4 by titration	H_2SO_4 by calculation
101	----------	0.0378	----------	----------
102	----------	.0033	----------	0.0034
104	0.1308	.4092	0.2104	----------
109	----------	----------	[a] .0080	----------
113	----------	----------	.23	----------
114	.6622	1.436	.3629	.450
115*b*	.6867	1.498	.4682	.478
115*c*	.6475	1.526	.5134	.560
116	.7330	1.512	.3617	.417
117	.2387	----------	.2862	----------
120*a*	----------	----------	.0932	----------
120*b*	----------	----------	.1125	----------
121	.0165	.8809	.729	----------
122	.4008	.7704	.144	.174
123	.3425	1.2878	.777	.786
125	1.391	2.604	.509	.50
[b] 127	.329	.775	.263	.29
[b] 128	.1810	.4013	.1051	.129
132*a*	.0069	.1138	----------	----------
132*b*	.0225	.1005	.078	.070
138	.0896	.3180	----------	----------

[a] SO_4'' only.

[b] Silica tube.

TABLE 11.—*Calculation of weights that reacted, based on preceding data*

[All weights in grams]

Experiment No.	$CuSO_4$ in final solution[a]	$CuSO_4$ that reacted	Cu_2S in residue	Cu_2S that reacted	SO_4'' combined with copper in solution	Balance of SO_4''	Equivalent weight of H_2SO_4	H_2SO_4 formed
102			0.2941	0.0059		0.0033	0.0034	0.0034
108			.0750	.0050				
114	1.665	0.255	.1048	.0552	0.996	.441	.450	.110
115*b*	1.725	.195	.1118	.0482	1.030	.468	.478	.138
115*c*	1.626	.293	.0780	.0820	.975	.550	.560	.220
116	1.841	.078	.1291	.0309	1.103	.409	.417	.077
117	.5998	.0402	.1267	.0333				
122	1.005	.210	.268	.052	.604	.167	.170	.170
123	.860	.099	.260	.060	.515	.773	.789	.089
125	3.50	.30	.311	.189	2.10	.51	.52	.180
127	.773	.442	.044	.116	.495	.28	.29	.29
128	[b].455	[b].455	[b].172	[b].172	.274	.127	.129	[c].38
132*a*	.0169	[b].0158	[b].0021	[b].0021	.0100	.104	.106	[c].017
132*b*	.0565	[b].0565	[b].0323	[b].0323	.0340	.068	.070	[c].053
138	.2251				.1335	.1825	.1862	[c].183

[a] Including Cu_2SO_4. [b] Formed. [c] That reacted.

TABLE 12.—*Molecular ratios of reacting substances*

Milligram-molecules

Experiment No.	Temperature (°C.)	$CuSO_4$	Cu_2S	Cu	H_2SO_4
114	250	1.60	0.347	0.920	1.12
115*b*	300	1.22	.30	1.70	1.40
115*c*	300	1.84	.515	2.36	2.25
116	250	.489	.194	1.05	.79
117	250	.252	.209	.564	
122	300	1.31	.33	1.98	1.73
123	300	.62	.38	1.06	.91
125	300	1.88	1.19	4.01	1.84
127	350	2.77	.729	3.52	2.95
128	350	2.85	1.08	5.44	3.88
132*b*	300	.35	.20	.76	.54

Molecular ratios

114	250	4.6	1	2.7	3.2
115*b*	300	4.1	1	5.7	4.6
115*c*	300	3.57	1	4.58	4.38
116	250	2.5	1	5.4	4.07
117	250	1	1	3	
122	300	4.0	1	6.0	5.3
123	300	1.6	1	2.8	2.4
125	300	1.6	1	3.4	1.5
127	350	3.8	1	4.83	4.06
128	350	2.6	1	5.02	3.6
132*b*	300	1.7	1	3.5	2.7
Theory for reactions (36) or (17)		3	1	5	4

TABLE 13.—*Solubility of cuprous chloride in calcium chloride solutions at 25° C.*

[Concentrations in per cent by weight]

Experiment No.	Specific gravity of solution	$CaCl_2$	CuCl
153	1.04	3.33	0.438
152	1.12	9.75	1.934
149	1.17	13.48	3.698
151	1.30	19.84	8.503
150	1.48	25.55	19.71

TABLE 14.—*Reaction of CuCl on FeO in aqueous solution at 100° C.*

[All weights in grams]

	Volume (cubic centimeters)	Fe taken as FeO	Cu taken as CuCl	Cu precipitated	Fe dissolved
Experiment 159*b*	139	0.141	0.324	0.092	0.074
Experiment 159*d*	196	.141	.444	.090	.047
Experiment 159*g*	200	.141	.444	.087	.047
Theory for equation (71)	----------	.141	.107	.107	.047
Theory for equation (72)	----------	.141	.321	.321	.141
Theory for equation (73)	----------	.141	.080	.080	.035
Experiment 159*c*	144	.141	.111	.081	.040
Theory for equation (71)	----------	.141	.107	.107	.047
Theory for equation (72)	----------	.049	.111	.111	.049
Theory for equation (73)	----------	.141	.080	.080	.035
Experiment 159*e*	200	.282	.160	.155	.080
Theory for equations (71), (72), and (73)	----------	.211 .070 .281	.160	.160	.070
Experiment 159*f*	187	[a] None.	.444	[b] .009	----------

[a] Metallic copper taken in excess in place of FeO.

[b] Cu dissolved.

TABLE 15.—*Reaction of CuCl and $FeCl_2$ at 100° in solutions of regulated pH value*

[Final volume of solution, 200 cubic centimeters]

Experiment No.	NaCl (grams)	Normal CH_3COOH (cubic centimeters)	Normal CH_3COONa (cubic centimeters)	pH at 25° C.	0.504 M $FeCl_2$ (cubic centimeters)	0.926 M CuCl (cubic centimeters)	Results
160*a*	2.20	20.0	20.0	4.5	1.7	4.8	No precipitate.
160*b*	1.97	16.0	24.0	4.7	1.7	4.8	Do.
160*c*	1.50	8.0	32.0	5.20	1.7	4.8	Very slight precipitate after some time.
160*d*	2.08	5.0	35.0	5.38	2.0	5.0	A faint cloud appeared in 2 minutes, a considerable film on glass in 2 hours with small crystals of Cu.
160*e*	1.08	3.2	36.8	5.62	2.0	5.0	Precipitation began at once and was too rapid for the formation of many recognizable crystals of Cu.
160*f*	.43	5.0	35.0	5.45	5.0	2.0	Precipitation fairly rapid.
160*g*	.43	8.0	32.0	5.23	5.0	2.0	Precipitation but no crystals of Cu seen.
160*h*	.43	10.0	30.0	5.08	5.0	2.0	Do.
160*i*	1.30	12.0	28.0	4.93	5.0	2.0	No Cu in 2 hours.
160*j*	2.17	5.0	35.0	5.38	5.0	2.0	Visible crystals of Cu on walls of flask in 2 hours.

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